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ETHYLENE

AUGUST 1984

Canada

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

ETHYLENE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

August 1984

FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGMENTS

The final version was prepared by the staff of the Environmental Protection Service who provided extensive revision to the text, drafted illustrations and incorporated all comments and additions. The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The draft of this manual was prepared under contract with Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation and Waterloo Engineering Limited.



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1 SUMMARY

ETHYLENE (C₂H₄)

Colourless gas with a sweet odour

SYNONYMS

Ethene, Bicarburretted Hydrogen, Elayl, Liquid Ethylene, Olefiant Gas

IDENTIFICATION NUMBERS

UN No. 1962 (compressed gas), 1038 (refrigerated liquid); CAS No. 74-85-1; OHM-TADS No. 7216713; STCC No. 4905734

GRADES & PURITIES

Commercial, 99.8 percent

Polymerization, 99.9 percent

Chemical, 92-95 percent

IMMEDIATE CONCERNS

Fire: Extremely flammable

Human Health: Low toxicity by all routes

Environmental: Harmful to certain terrestrial plants

PHYSICAL PROPERTY DATA

Shipping State: gas or liquid, under pressure

State (15°C, 1 atm): gas

Boiling Point: -103.7°C

Melting Point: -169.2°C

Flammability: flammable

Vapour Pressure: 4040 kPa (-1.5°C)

Specific Gravity of Vapour: 0.97 (25°C)

Specific Gravity of Liquid: 0.566 g/mL (-103.7°C)

Solubility (in water): insoluble

Behaviour (in water): floats, boils and evaporates

Behaviour (in air): vapour clouds initially follow ground

Odour Threshold Range: 260-700 ppm

ENVIRONMENTAL CONCERNS

Gas will disperse quite rapidly. There is no bioaccumulation or food chain contamination potential. Ethylene in excess of 0.1 ppm will injure sensitive plants.

HUMAN HEALTH

TLV®: simple asphyxiant

IDLH: not established

Exposure Effects

Inhalation: Vapours are not irritating to eyes, nose or throat. Low toxicity by inhalation. If inhaled in high concentrations, causes headache, drowsiness, dizziness, nausea, vomiting, narcosis and loss of consciousness. Moderate concentration in air causes unconsciousness

Contact: Liquid will cause frostbite to skin, and pain and frost burns to eyes

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "FLAMMABLE". Call fire department and notify manufacturer. Eliminate sources of ignition including traffic and equipment. Stop the flow if safe to do so. Avoid contact with liquid and inhalation of vapour; stay upwind of release.

Fire Control

Do not extinguish fire unless release can be stopped. Use foam, dry chemical, carbon dioxide or water fog to extinguish. Flashback may occur along vapour trail. Cool fire-exposed containers with water. Stay clear of tank ends.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Allow vapours to disperse. Keep ignition sources away until concentrations have decreased

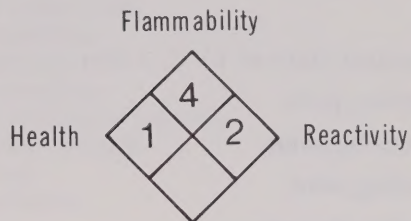
Water: Large concentrations of ethylene in water are unlikely. Under most circumstances, ethylene can be removed by aeration

Air: Vapour cloud will disperse. Water sprays used to disperse the cloud may assist in lowering the concentration

NAS HAZARD RATING

<u>Category</u>	<u>Rating</u>
Fire.....	4
Health	
Vapour Irritant.....	0
Liquid or Solid Irritant.....	0
Poison.....	1
Water Pollution	
Human Toxicity.....	0
Aquatic Toxicity.....	1
Aesthetic Effect.....	0
Reactivity	
Other Chemicals.....	1
Water.....	0
Self-reaction.....	2

NFPA HAZARD CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Colourless gas (HCG 1981)
Usual shipping state(s)	Liquid: Shipped at 20°C under 8620 kPa pressure. At 10°C, the gas is liquefied under these pressures (HCG 1981) or shipped at 4 482 kPa and lower temperatures (Ethylene 1980)
Physical state at 15°C, 1 atm	Gas
Melting point	-169.2°C (CRC 1980; Kirk-Othmer 1980)
Freezing point	-181°C (CRC 1980)
Boiling point	-103.71°C (Kirk-Othmer 1980; Ullmann 1975)
Vapour pressure	4040 kPa (-1.5°C) (CRC 1980)

Densities

Density	Gas: 1.2603 g/L (25°C) (Ullmann 1975) 1.261 g/L (0°C) (Matheson 1980) Liquid: 0.566 g/mL (-103.7°C) (Kirk-Othmer 1980; Ullmann 1975)
Vapour specific gravity	0.978 (0°C) (HCG 1981) 0.97 (25°C) (Ullmann 1975)

Fire Properties

Flammability	Flammable gas (NFPA 1978)
Autoignition temperature	425°C (Ullmann 1975) 450°C (NFPA 1978) 490°C (Kirk-Othmer 1980)
Burning rate	7.4 mm/min (CHRIS 1978)
Upper flammability limit	36 percent (v/v) (NFPA 1978; Kirk-Othmer 1980) 28.5 percent (v/v) (Ullmann 1975)
Lower flammability limit	2.7 percent (v/v) (NFPA 1978; Kirk-Othmer 1980)
Burning characteristics	Burns with a luminous flame (Merck 1976)
Heat of combustion	1411 kJ/mole (HCG 1981; Kirk-Othmer 1980)
Combustion products	Carbon dioxide and water (CRC 1980)
Explosiveness	Under extreme conditions involving high temperatures and pressure, decomposes into its elements especially when activated by shock (Kirk-Othmer 1980)

Electrical ignition hazard

May be ignited by static discharge

Other Properties

Molecular weight of pure substance

28.0536 (Kirk-Othmer 1980)

Constituent components of typical commercial grade

99.8 percent ethylene
0.1 percent (max.) methane
0.2 percent (max.) ethane (Pike 1981)

Constituent components of typical polymerization grade

99.9 percent ethylene
Maximum impurities:
200 ppm methane
200 ppm ethane
10 ppm propylene
4 ppm C_4 and higher alkenes
5 ppm carbon dioxide
5 ppm water
5 ppm methanol
2 ppm oxygen
2 ppm acetylene
2 ppm chlorine
5 ppm all others (Kirk-Othmer 1980)

Constituent components of typical chemical grade

92-95 percent ethylene
Maximum impurities:
<5-8 percent ethane and propane
<0.2 percent C_4 and higher alkenes
100 ppm propylene
100 ppm higher acetylenes
10 ppm acetylene
50 ppm water
10 ppm carbon dioxide and monoxide

Refractive index

1.363 (100°C) (CRC 1980)

Viscosity

Gas: 0.01 mPa•s (20°C) (CRC 1980)
Liquid: 0.161 mPa•s (-103.71°C) (Kirk-Othmer 1980)

Latent heat of fusion

3.35 kJ/mole (-169.15°C) (Kirk-Othmer 1980)

Latent heat of vaporization

13.54 kJ/mole (-103.71°C) (Kirk-Othmer 1980)

Heat of formation

52.47 kJ/mole (25°C) (JANAF 1971)

Entropy

0.220 kJ/(mole•K) (25°C) (Ullmann 1975)

Ionization potential

10.51 eV (Rosenstock 1977)

Heat capacity

constant pressure (C_p)

Liquid: 2.4647 J/(g•°C) (-103.71°C) (Matheson 1980)
Gas: 1.548 J/(g•°C) (25°C) (Matheson 1980)

constant volume (C_V)	Gas: 1.244 J/(g•°C) (Matheson 1980)
C_p/C_V (γ)	Gas: 1.244 (Matheson 1980)
Critical pressure	5117 kPa (HCG 1981) 5042 kPa (Kirk-Othmer 1980)
Critical temperature	9.9°C (HCG 1981) 9.2°C (Kirk-Othmer 1980)
Triple point	-169.19°C, 0.11 kPa (Kirk-Othmer 1980)
Coefficient of thermal expansion	$3.7 \times 10^{-3}/^{\circ}\text{C}$ (20°C) (Perry 1973)
Thermal conductivity	0.01778 W/(m•K) (0°C) (Matheson 1980)
Surface tension	16.4 mN/m (liquid at -103.71°C) (Kirk-Othmer 1980)
Log ₁₀ octanol/water partition coefficient	1.13 (Hansch and Leo 1979)

Solubility

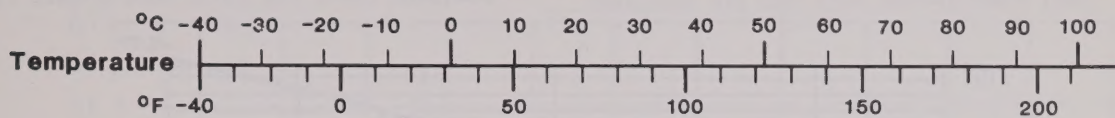
In water	0.028 g/100 g (0°C) (Gas Data 1974)
In other common materials	Decomposes slightly in ethanol, acetone and benzene. Soluble in diethyl ether (CRC 1980). The following solubilities are given:

<u>Solvent</u>	<u>Volume gas/ volume solvent</u>
carbon tetrachloride	3.9
acetone	3.8
benzene	3.6
methyl acetate	3.7
chlorobenzene	3.0
ethanol	2.7
	(Gas Data 1974)

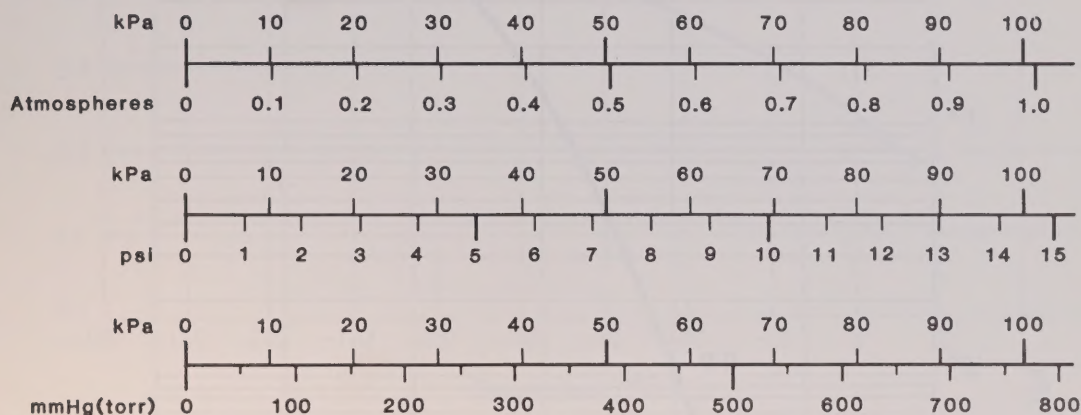
Vapour Weight to Volume Conversion Factor	1 ppm = 1.164 mg/m ³ (20°C) (Verschuieren 1977)
---	--

ETHYLENE

CONVERSION NOMOGRAMS



Pressure 1 kPa = 1,000 Pa



Viscosity

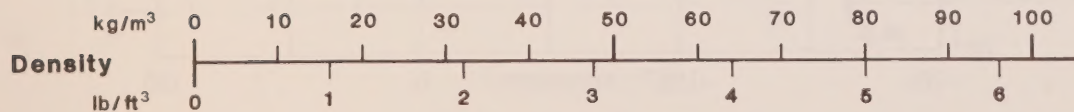
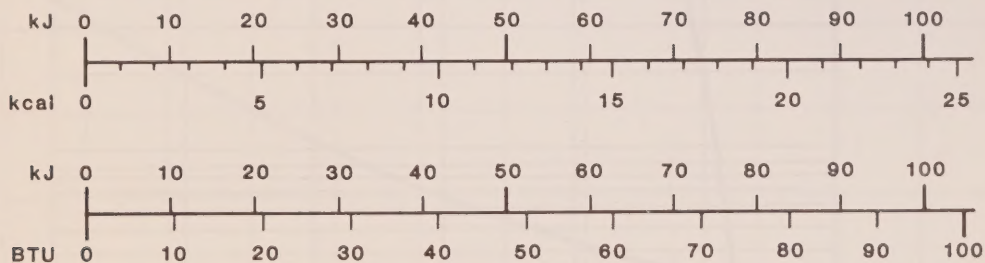
Dynamic 1 Pa·s = 1,000 centipoise (cP)

Kinematic 1 m^2/s = 1,000,000 centistokes (cSt)

Concentration (in water)

1 ppm $\approx$ 1 mg/L

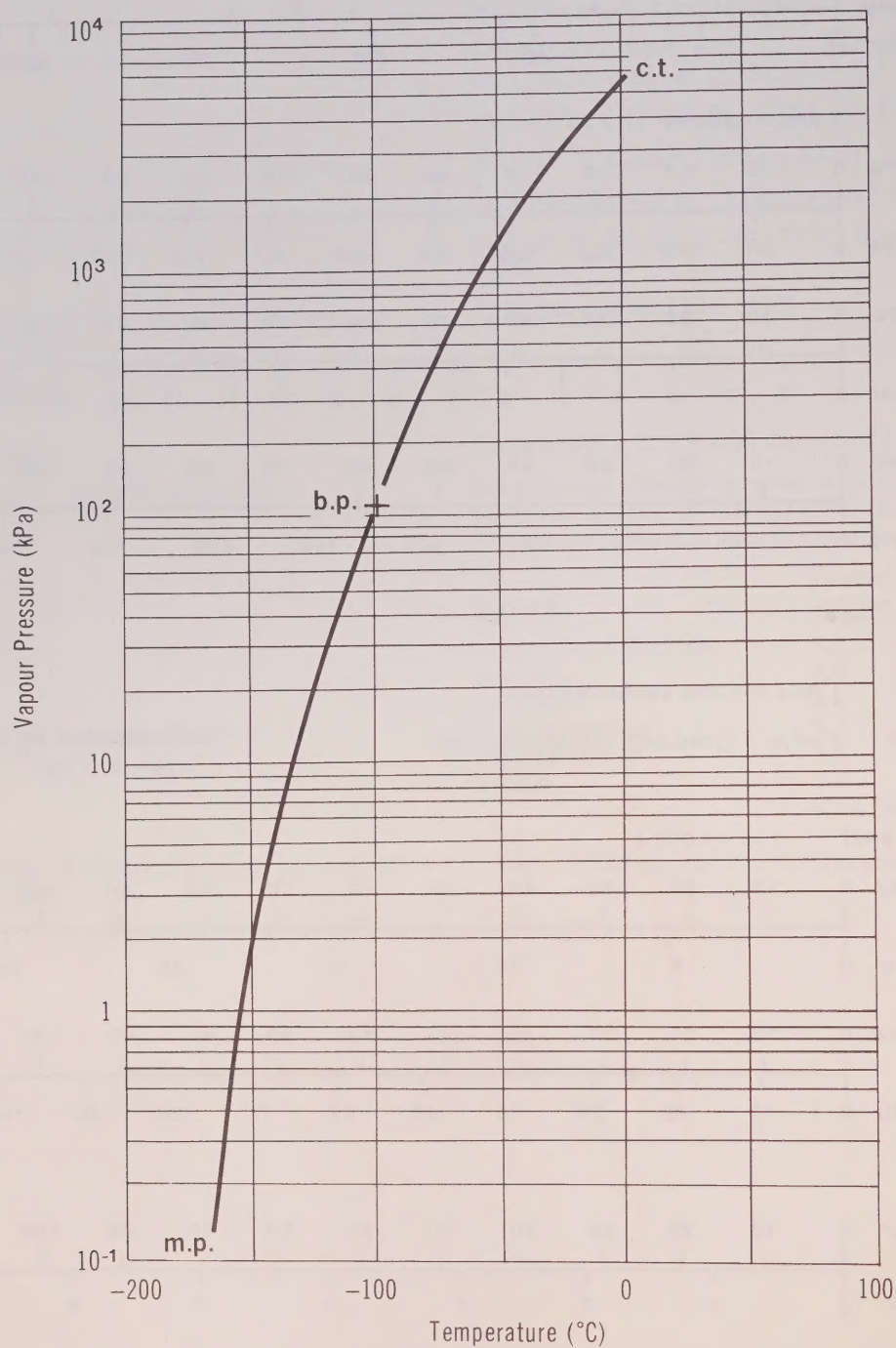
Energy (heat) 1 kJ = 1,000 J



ETHYLENE

VAPOUR PRESSURE vs TEMPERATURE

Reference: Chem. Eng. 1975; KIRK-OTHMER 1980



ETHYLENE

LIQUID DENSITY vs TEMPERATURE

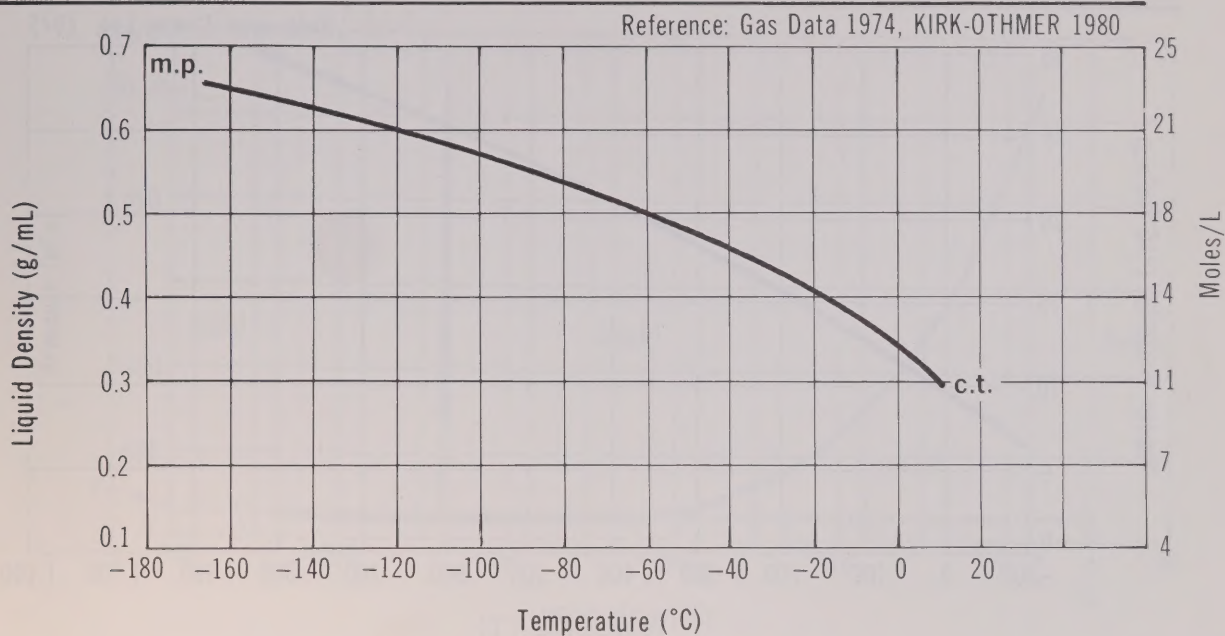
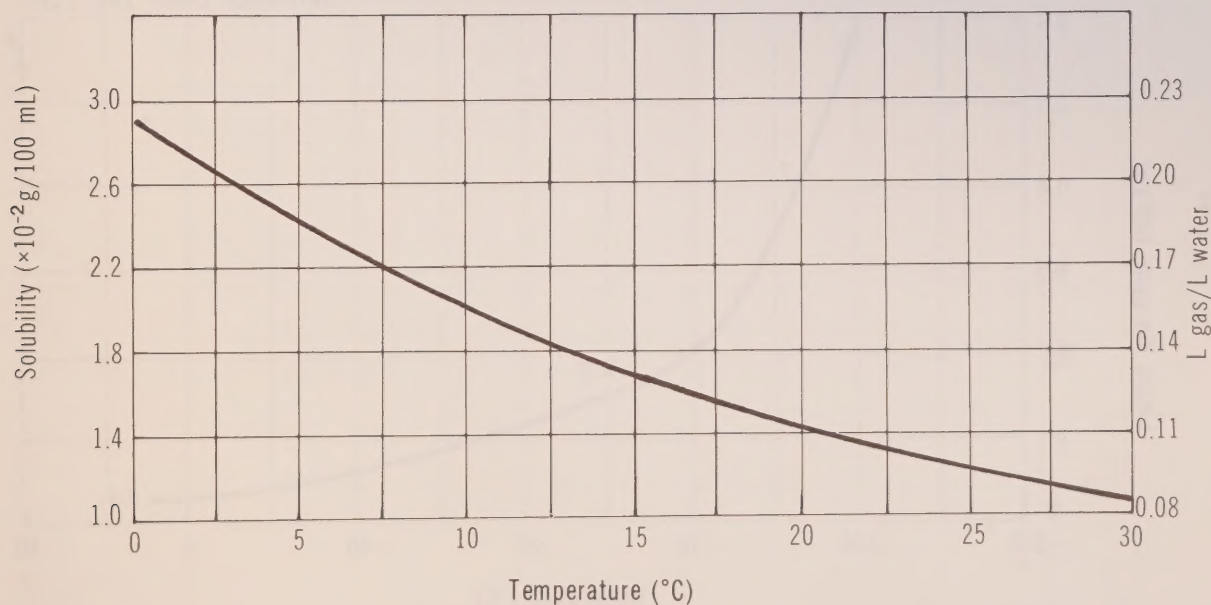


FIGURE 3

ETHYLENE

SOLUBILITY IN WATER vs TEMPERATURE



ETHYLENE

VAPOUR VISCOSITY vs TEMPERATURE

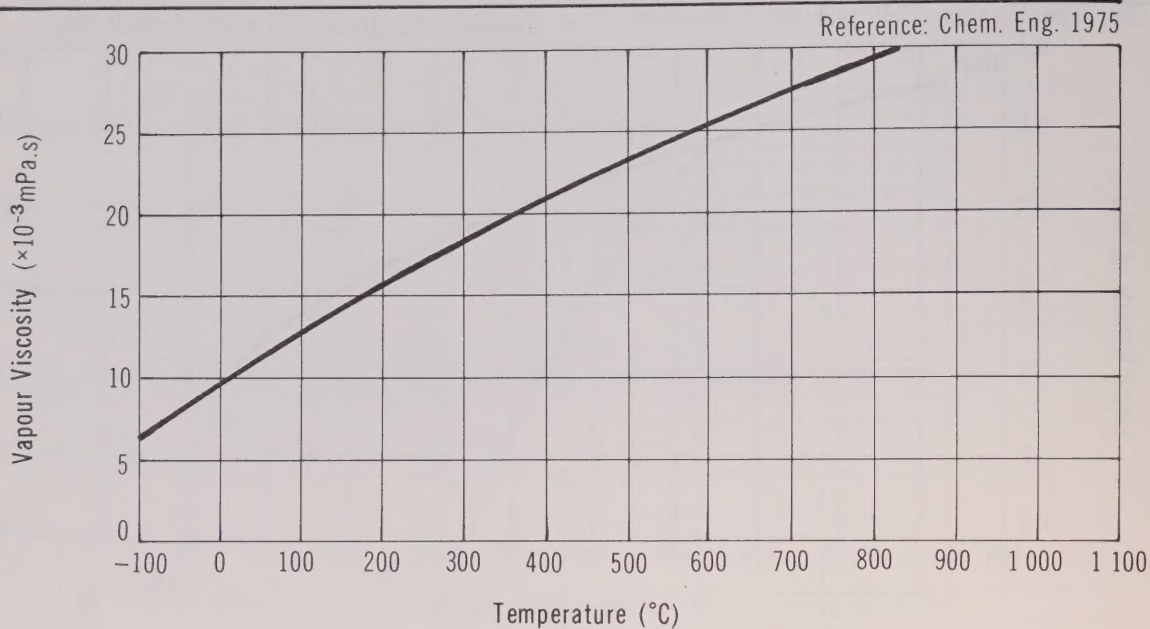
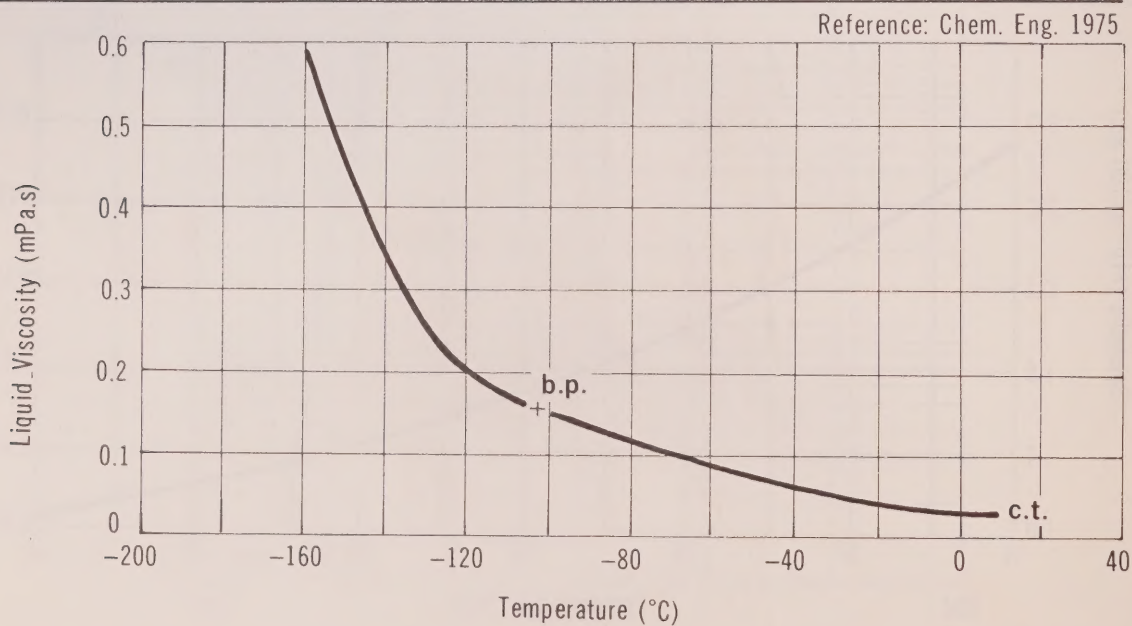


FIGURE 5

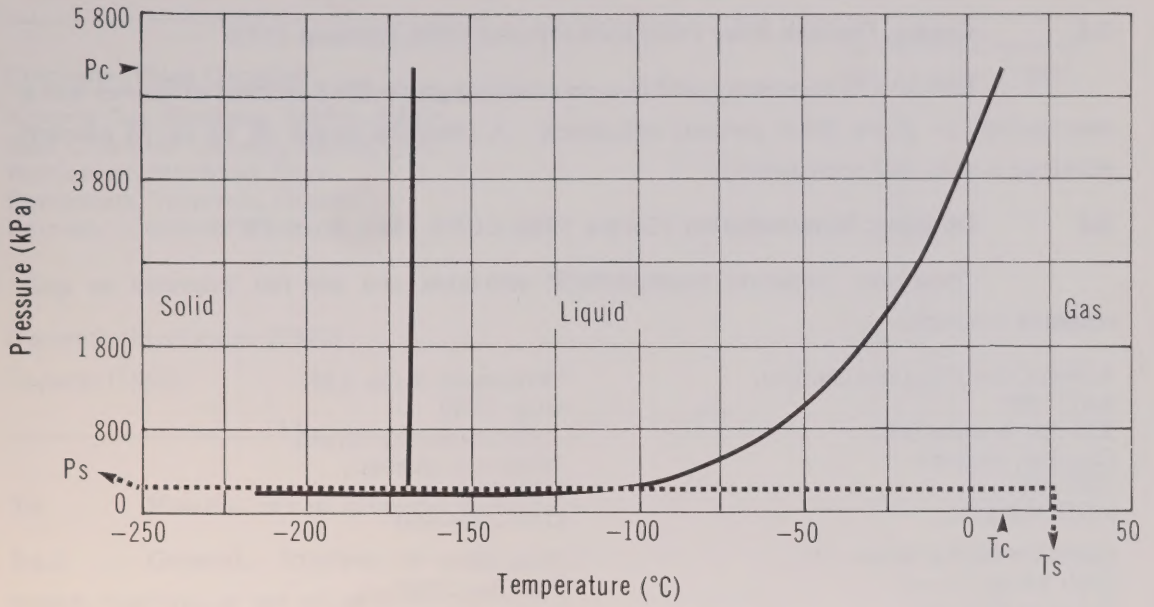
ETHYLENE

LIQUID VISCOSITY vs TEMPERATURE



ETHYLENE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Pike 1981; Kirk-Othmer 1980; Ullmann 1975)

Ethylene is commonly sold in a commercial grade (99.8 percent ethylene) and a polymerization grade (99.9 percent ethylene). A chemical grade of 92 to 95 percent ethylene is also sold occasionally.

3.2 Domestic Manufacturers (Corpus 1983; CCPA 1981; Scott 1979)

These are corporate headquarters' addresses and are not intended as spill response contacts.

Alberta Gas Ethylene Co. Ltd.
Suite 500
333-5th Avenue S.W.
Calgary, Alberta
T2P 3B6
(403) 263-8130

Esso Chemical Canada
2300 Yonge Street
Toronto, Ontario
M5W 1K3
(416) 488-6600

Petromont & Co. Ltd.
Suite 2000
2020 University Street
Montreal, Quebec
H3A 2A5
(514) 282-9091

Petrosar
P.O. Box 3060
Sarnia, Ontario
N7T 7M1
(519) 862-2911

3.3 Other Suppliers (Corpus 1983; Scott 1979)

Dow Chemical Canada Inc.
P.O. Box 1012
Modeland Drive
Sarnia, Ontario
N7T 7K7
(519) 339-3131

Dupont Canada Inc.
St. Clair River Works
Corunna, Ontario
N0N 1G0
(519) 862-1445

3.4 Major Transportation Routes

Current Canadian production of ethylene is located in Ontario, at Sarnia and Corunna (46 percent of total production); in Alberta, at Joffre (35 percent of total production); and in Quebec, at Varennes and Montreal. The product is primarily shipped via pipeline direct to users in one of the three areas noted. Some product from Sarnia is shipped via tank truck to the United States via Blue Water Bridge (CCPA 1982).

3.5 Production Levels (Corpus 1983)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Alberta Gas Ethylene, Joffre, Alta.	540
Esso Chemical Canada, Sarnia, Ont.	260
Petromont, Montreal, Que.	75
Petromont, Varennes, Quebec	225
Petrosar, Corunna, Ont.	450
TOTAL	1550
Domestic Production (1982)	1013
Imports (1982)	0.1
TOTAL SUPPLY	1013.1

3.6 Manufacture of Ethylene (Shreve 1977; CCPA 1982; Kirk-Othmer 1980)

3.6.1 General. Ethylene is made in Canada by the cracking of propane, ethane, butane, naphtha, or gas oil, or from the separation of refinery gas.

3.6.2 Raw Materials. A variety of hydrocarbon feedstocks are used, as noted above.

3.6.3 Manufacturing Process. In the cracking (or pyrolysis) process, propane, ethane, butane, naphtha, or gas oil feedstock, diluted with steam, is in a cracking unit, at temperatures in the 700-900°C range, for about 30-600 milliseconds. The product may contain about one-third ethylene, with many other co-products. This is then fractionated to separate unreacted feedstock which is recycled.

Refinery gas contains a variable amount of ethylene (in the order of 5 to 10 percent). The ethylene is separated from the other components by fractionation.

3.7 Future Development (Corpus 1983; CCP 1981)

Alberta Gas Ethylene had its second cracking plant (AGE-2) on-stream in mid-1984 at Joffre, Alberta (capacity of 680 kt/yr). A third plant (AGE-3) is tentatively planned for late 1986 (capacity of 680 kt/yr).

3.8 Major Uses in Canada (Corpus 1983)

Ethylene is used in the manufacture of polyethylene, ethylene oxide, ethylene dichloride, ethylbenzene, ethanol and ethyl chloride. In 1982, 54 percent of ethylene was

used in the production of polyethylene, 17 percent for ethylene oxide, 16 percent for ethylene dichloride and 9 percent for ethylbenzene.

3.9 Major Buyers in Canada (Corpus 1983; CBG 1980)

Celanese Canada, Edmonton, Alta.

C-I-L, Edmonton, Alta.

Commercial Alcohols, Varennes, Que.

Dow Chemical Canada, Sarnia, Ont.

Du Pont Canada, Corunna, Ont.

Ethyl Canada, Corunna, Ont.

Hercules Canada, Varennes, Que.

Polysar, Sarnia, Ont.

Shell Canada Chemical, Corunna, Ont.

Union Carbide Canada, Montreal, Que; Corunna, Ont.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 General. The most common means of transporting ethylene is by pipeline. Ethylene gas is transferred in this way by special centrifugal or reciprocating compressors. Insignificant amounts compared to pipelines are transported by tank trucks or railway tank cars, the main reason for this being the cost involved to control and prevent excessive tank pressure (Pike 1981; Ethylene 1980).

Cylinders are used for small quantities of ethylene. Some specially designed ships are also used to transport ethylene, although they currently do not call on Canadian ports.

4.1.2 Railway Tank Cars. Railway transport of ethylene is only allowed with special permission using special tank cars designated 113C120W. These cars have a tank constructed of 304 stainless steel with an outer shell of steel. The annulus between tanks is filled with perlite and is evacuated to a pressure of about 0.01-0.1 kPa (0.07-0.7 psi). The typical capacity of these tank cars is a maximum payload of 63.3 tonnes, with an empty weight of 52.6 tonnes. The ethylene is transported as a super-cooled liquid at pressures below 380 kPa (55 psi) (Ethylene 1980).

4.1.3 Tank Motor Vehicles. Tank motor vehicles carrying liquefied ethylene require special permit. The ethylene is again carried as a super-cooled liquid in a double-walled tank with the annulus evacuated. A small fleet of tank trucks is currently transporting liquefied ethylene from Sarnia to the United States via the Blue Water Bridge. These vehicles have a light weight of 15 tonnes and a maximum payload of 20 tonnes. The maximum operating pressure is about 324 kPa (47 psi) (Ethylene 1980).

4.1.4 Cylinders. Cylinders permitted under the Canadian Transport Commission Regulations are listed in Table 2. Ethylene in cylinders is a liquid under high pressure. Cylinders are typically used to transport small quantities such as for laboratory usage. Cylinders are equipped with a Compressed Gas Association standard valve outlet Number 350, with a thread size of 0.825 inch left-hand external thread accepting a round nipple. Lecture bottles (1.5-3 kg capacity) have a special 5/16 inch, 32 threads per inch, final outlet and a 9/16 inch, 18 threads per inch, male outlet (Matheson 1980).

TABLE 2 CYLINDERS FOR ETHYLENE SERVICE (RTDCR 1974)

CTC/DOT Number	Specification Summary
3A1800 3AA 1800	Seamless steel cylinder, capacity not over 1000 lb. water equivalent, maximum fill density 31.0 percent, service pressure 12 400 kPa (1800 psi)
3A 2000 3AA 2000	As above except 32.5 percent fill density, service pressure 13 800 kPa (2000 psi)
3A 2400 3AA 2400	As above except 35.5 percent fill density, service pressure 16 600 kPa (2400 psi)
3E 1800	Seamless steel cylinder, capacity not over 1000 lb. water equivalent, fill density 31.0 percent, service pressure 12 400 kPa (1800 psi)
39	Nonreuseable, not refillable cylinder, steel constructed of seamless tube of specified content, service pressures and fill densities correspond as in the above specifications

4.1.5 Pipelines. Most ethylene is currently transported by pipeline. The critical temperature of ethylene is about 9.9°C, very near to ambient soil temperatures; thus, to avoid two-phase flow as well as heat loss, ethylene is transmitted in the vapour phase. Pipelines are operated in two modes, subcritical or supercritical, corresponding to the pressure range above or below the critical pressure of about 5100 kPa (740 psi). In either case, condensation into liquid by small pressure drops or increases is avoided. The subcritical lines operate at pressures of 2000 to 4400 kPa (290-638 psi) and gas temperatures from 0 to 20°C. At these conditions, the gas has a density of 27 to 100 kg/m³. The supercritical pipelines operate at pressures of 5400 to 9800 kPa (780-1420 psi) and gas temperatures of 2 to 20°C. The corresponding gas densities vary from 200 to 400 kg/m³. The transport capability of the supercritical mode is much more than the subcritical mode, corresponding roughly to the 5- to 8-fold gas density difference, and thus is the most common operation mode for ethylene pipelines (Ethylene 1980).

4.2 Storage

Plants frequently store ethylene in specially designed tanks conforming to API Specification 620, Appendix Q. These cryogenic tanks are constructed as a double envelope, with an inner liner of stainless or other nickel-containing steel and an outer

envelope of carbon steel. The space between the liners is insulated. Capacities vary, with the largest being 24 000 m³ (8.5 x 10⁵ ft.³) of liquid ethylene. Two configurations of such tanks are illustrated in Figure 7 (Ethylene 1980).

Manufacturers are also using underground salt domes and caverns for ethylene storage. For example, Dome has operated a subterranean cavern system at Midland, Michigan, since the late 1950s (Ethylene 1980; Kirk-Othmer 1980).

4.3 Compatibility with Materials of Construction

The compatibility of ethylene with materials of construction is indicated in Table 3. The unbracketed abbreviations are described in Table 4. The rating system for this report is briefly described below.

Recommended: This material will perform satisfactorily in the given application.

Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 3 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical Temp. (°C)	Material of Construction		
		Recommended	Not Conditional	Recommended
1. Pipes and fittings	most	Stainless Steel (Schedule 80) Nickel Alloys (DCRG 1978) Stainless Steel (304) (Pike 1981)	Carbon Steel (Pike 1981)	
2. Valves		Alloy Steel Cast Steel with PVC Lining (DCRG 1978)		
3. Tanks		5.0% Ni Steel (ASTM 645-74a) 5.5% Ni Steel		

ETHYLENE

STORAGE TANKS

Reference: Ethylene 1980

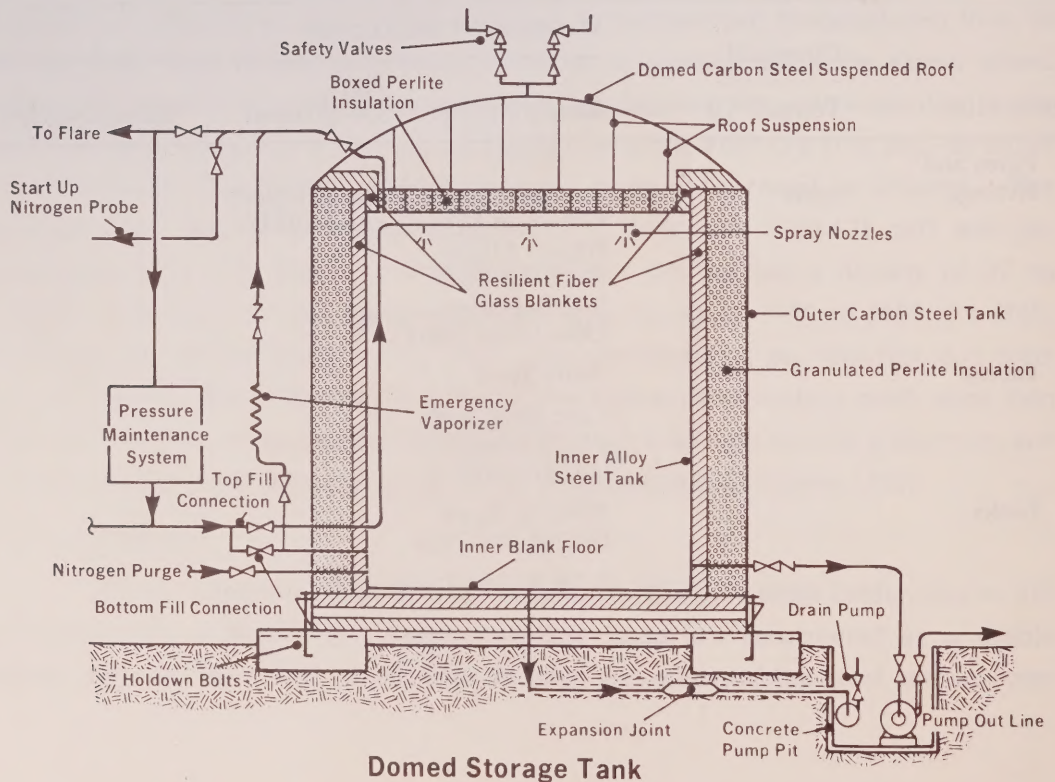
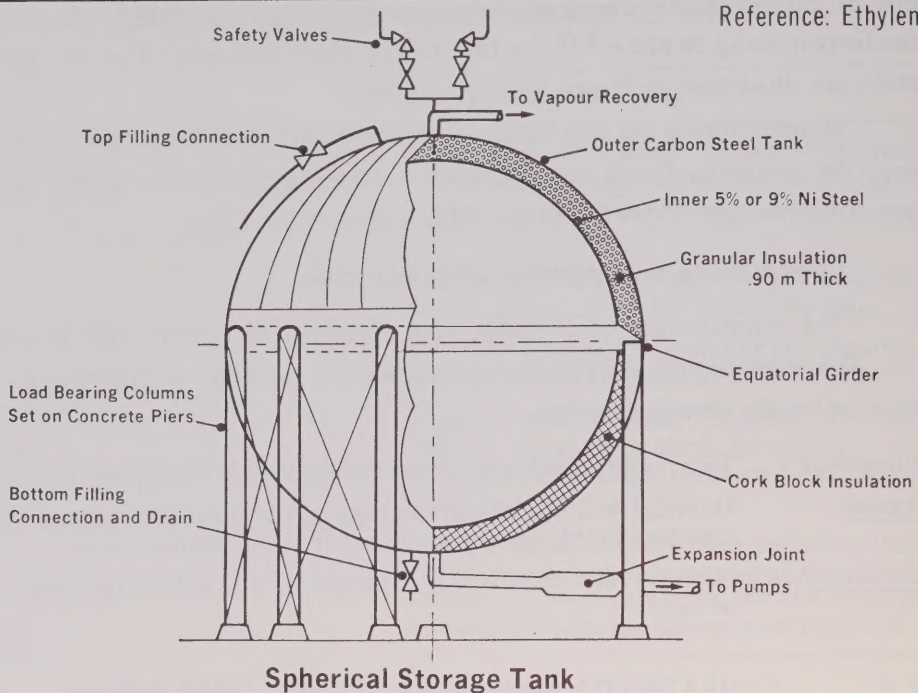


TABLE 3 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical	Material of Construction		
	Temp. (°C)	Recommended	Not Conditional	Recommended
3. Tanks (Cont'd)		9.0% Ni Steel (ASTM 353-64 and 353-65)		
		Stainless Steel (ASTM 240-304)		
		Aluminum (ASTM 209-5083-0) (Ethylene 1980)		
4. Others	24-100	Glass (CDS 1967)		
	24	Concrete Wood (CDS 1967)		
	66	PVDC (DCRG 1978)		
	79	PP (DCRG 1978)		
	107	Chlorinated Polyether (DCRG 1978)		
	135	PVDF (DCRG 1978)		

TABLE 4 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
	Aluminum
	Cast Steel
	Chlorinated Polyether
	Glass
	Nickel Alloys and Steel
PP	Polypropylene
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
SS (followed by grade)	Stainless Steel
	Wood

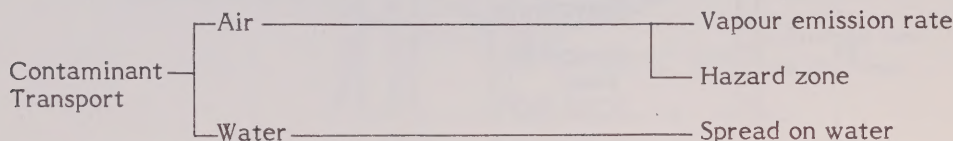
5 CONTAMINANT TRANSPORT

5.1 General Summary

Ethylene, when released into the environment, will rapidly disperse as a vapour cloud. The vapour cloud tends to hug the ground and spread while dispersing rather than lift off the ground and disperse rapidly into the upper atmosphere.

Ethylene released onto soil surfaces will vaporize. Adsorption onto the soil and downward transport of the liquid toward the groundwater table are not likely to cause environmental problems.

The following factors are considered for the transport of ethylene in the air and water media.



5.2 Leak Nomograms

As no significant quantities of ethylene are carried by railway tank cars or tank motor vehicles, no leak nomograms have been prepared.

5.3 Dispersion in the Air

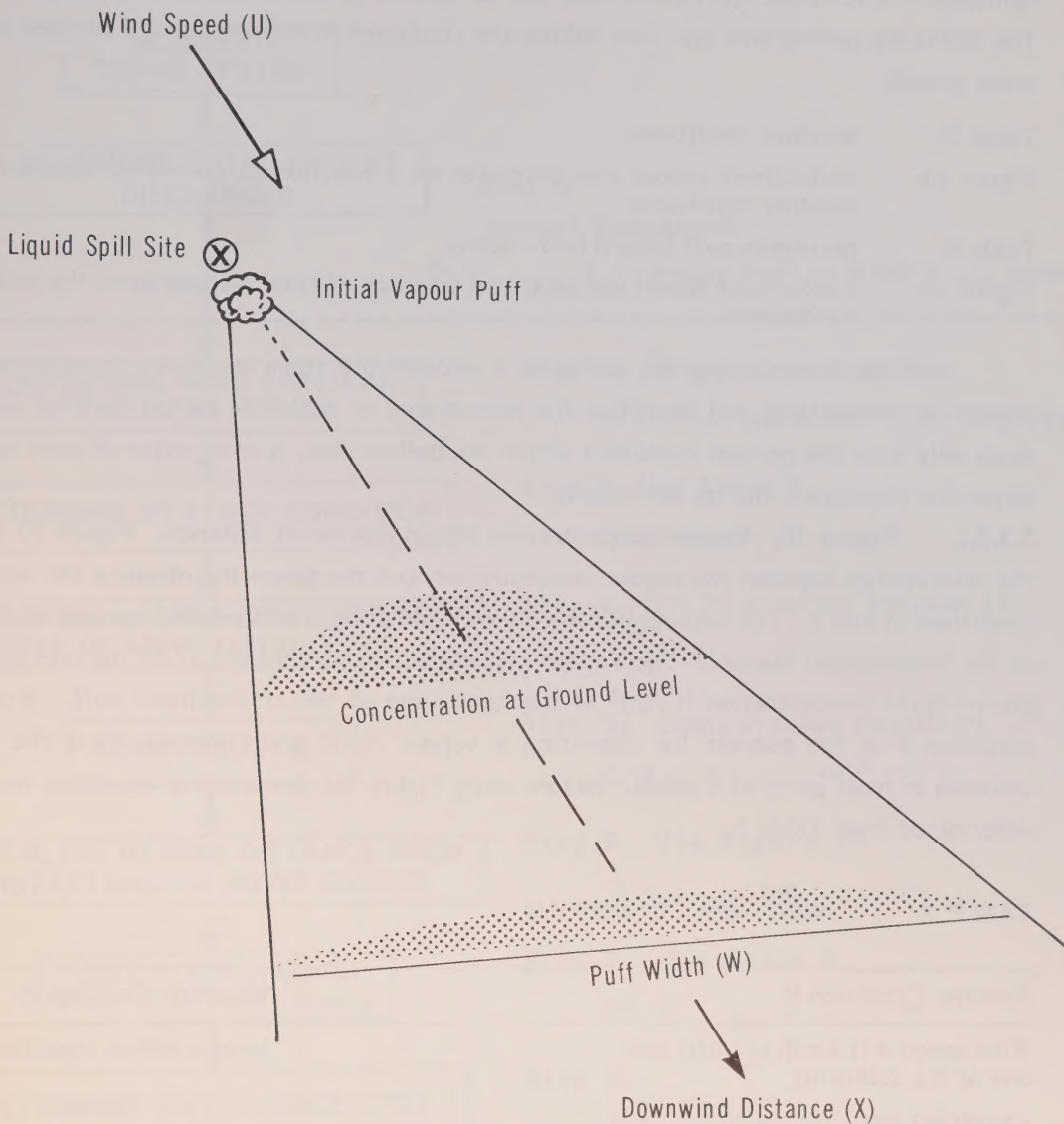
5.3.1 Introduction. Since liquefied ethylene under pressure is extremely volatile, vapour released from a liquid pool spilled on a ground or water surface evaporates rapidly enough to consider the spill as producing instantaneous vapour in the form of a puff. Also, ethylene as a gas can be treated as a puff.

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 8 depicts schematically the contaminant plume configuration from a "puff" surface release. The dispersion model represents the spill as an instantaneous point source (with a total vapour release quantity, Q_T) equal to the amount of contaminant spilled.

ETHYLENE

SCHEMATIC OF CONTAMINANT PUFF



5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in the order given):

Table 5: weather conditions

Figure 10: normalized vapour concentration as a function of downwind distance and weather conditions

Table 6: maximum puff hazard half-widths

Figure 12: vapour puff travel distance as a function of time elapsed since the spill and wind speed

The flow chart given in Figure 9 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 10: Vapour concentration versus downwind distance. Figure 10 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (C/Q_T) at the centreline of the contaminant puff. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 10, the weather condition must be determined from Table 5.

TABLE 5 WEATHER CONDITIONS

Weather Condition F	Weather Condition D
Wind speed <11 km/h (≈ 3 m/s) and one of the following - overcast day - night time - severe temperature inversion	Most weather conditions

ETHYLENE

FLOW CHART TO DETERMINE
VAPOUR HAZARD ZONE

ACCIDENT:
LIQUID SPILLED

DETERMINE TOTAL AMOUNT
DISCHARGED

Step 1:

Amount discharged:

$$Q_T = \text{..... L} \times \text{density (kg/L)} \div 1000 = \text{..... tonnes}$$

DETERMINE WIND SPEED (U)
AND DIRECTION (D)

Step 2: Observed or estimated

U = km/h; D = degrees

DETERMINE WEATHER CONDITION

Step 3: Use Table 5

Condition =

DETERMINE HAZARD CONCENTRATION
(C) - LOWER OF ASPHYXIATION LEVEL or LFL

Step 4: C = 35 g/m³ for Ethylene LFL

COMPUTE $C \div Q_T$

Step 5: Computation required

$$C/Q_T = \text{..... m}^{-3}$$

CALCULATE HAZARD DISTANCE FROM
INSTANTANEOUS POINT SOURCE

Step 6: Use Figure 10

X = km

CALCULATE HAZARD
HALF-WIDTH (W/2)_{max.}

Step 7: Use Table 6

(W/2)_{max.} = m

DETERMINE TIME (t) SINCE SPILL

Step 8:

t = s

CALCULATE DISTANCE (X_t) TRAVELLED
BY PUFF SINCE TIME (t) OF ACCIDENT

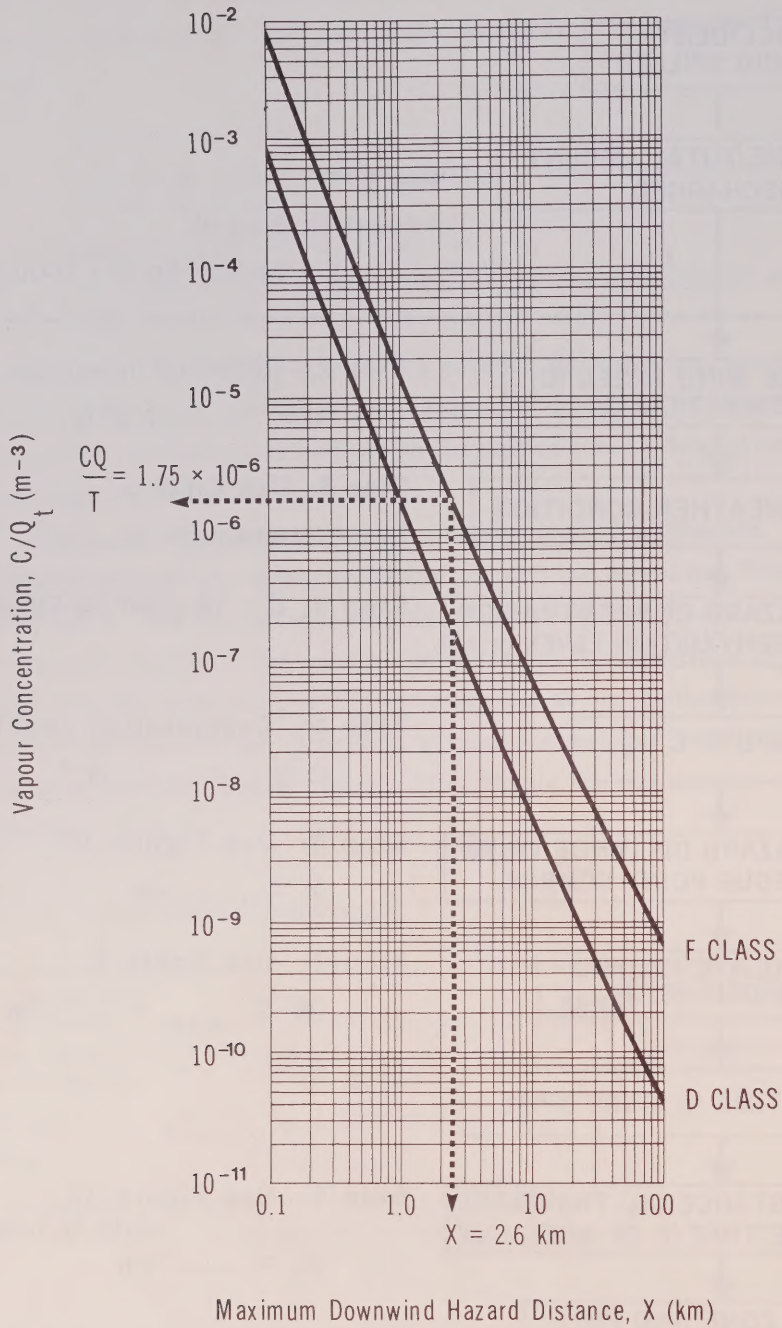
Step 9: Use Figure 12

with U from Step 2

X_t = km

HAZARD ZONE AND PUFF
LOCATION DEFINED

ETHYLENE

NORMALIZED VAPOUR CONCENTRATION
VS DOWNWIND DISTANCE

Use: The maximum hazard distance, X , downwind of the spill can be calculated from Figure 10 knowing:

- Q_T , the mass of vapour emitted (equivalent to liquid spilled)
- U , the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C , which is the lower value of 10 times the Threshold Limit Value® (TLV, in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3). For a simple asphyxiant, no TLV® value is pertinent. The concentration of contaminant that will lower the oxygen level to less than 18 percent v/v (asphyxiation level) is 14 percent v/v. Therefore, the lower of 14 percent v/v or the LFL is used. Note, to convert the LFL (in percent by volume) or the asphyxiation level (in percent by volume) to concentrations in g/m^3 , use Figure 11.

5.3.2.2 Table 6: Maximum puff hazard half-widths. This table presents data on the maximum puff hazard half-width, $(W/2)_{\text{max}}$, for a range of Q_T values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of the ethylene Lower Flammability Limit (LFL) of 35 g/m^3 . The maximum puff hazard half-width represents the maximum half-width of the ethylene vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of the LFL. Table 6 is therefore only applicable for an ethylene hazard concentration limit of the LFL, or 35 g/m^3 . Also, data are provided up to a maximum hazard distance downwind of 100 km.

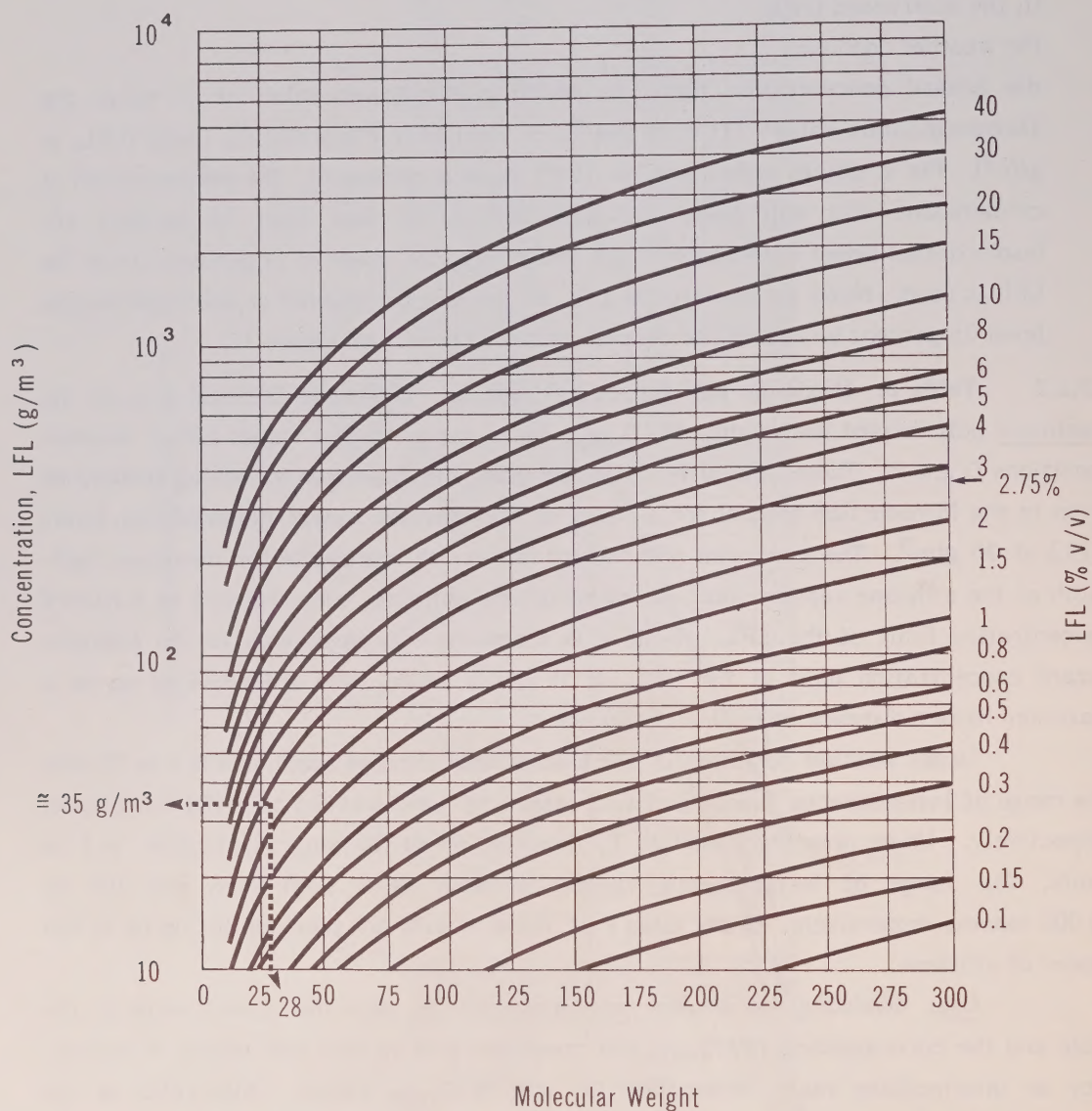
Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.5 to 1 100 000 tonnes, respectively. Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.5 to 50 000 tonnes, respectively. Under class F of Table 6, data are provided for up to 50 000 tonnes of ethylene.

Use: Knowing the weather condition and Q_T , pick the closest value in the table and the corresponding $(W/2)_{\text{max}}$, the maximum puff hazard half-width, in metres. (For an intermediate value, interpolate Q_T and $(W/2)_{\text{max}}$ values. Also refer to the example at the bottom of Table 6.

5.3.2.3 Figure 12: Puff travel time versus travel distance. Figure 12 presents plots of puff travel time (t) versus puff travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

ETHYLENE

CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m³)



Example: Ethylene, MW = 28, LFL = 2.75%, then LFL in g/m³ $\approx$ 35

Note: data applicable at 25°C and 760 mm Hg pressure

TABLE 6 MAXIMUM PUFF HAZARD HALF-WIDTHS (FOR ETHYLENE)

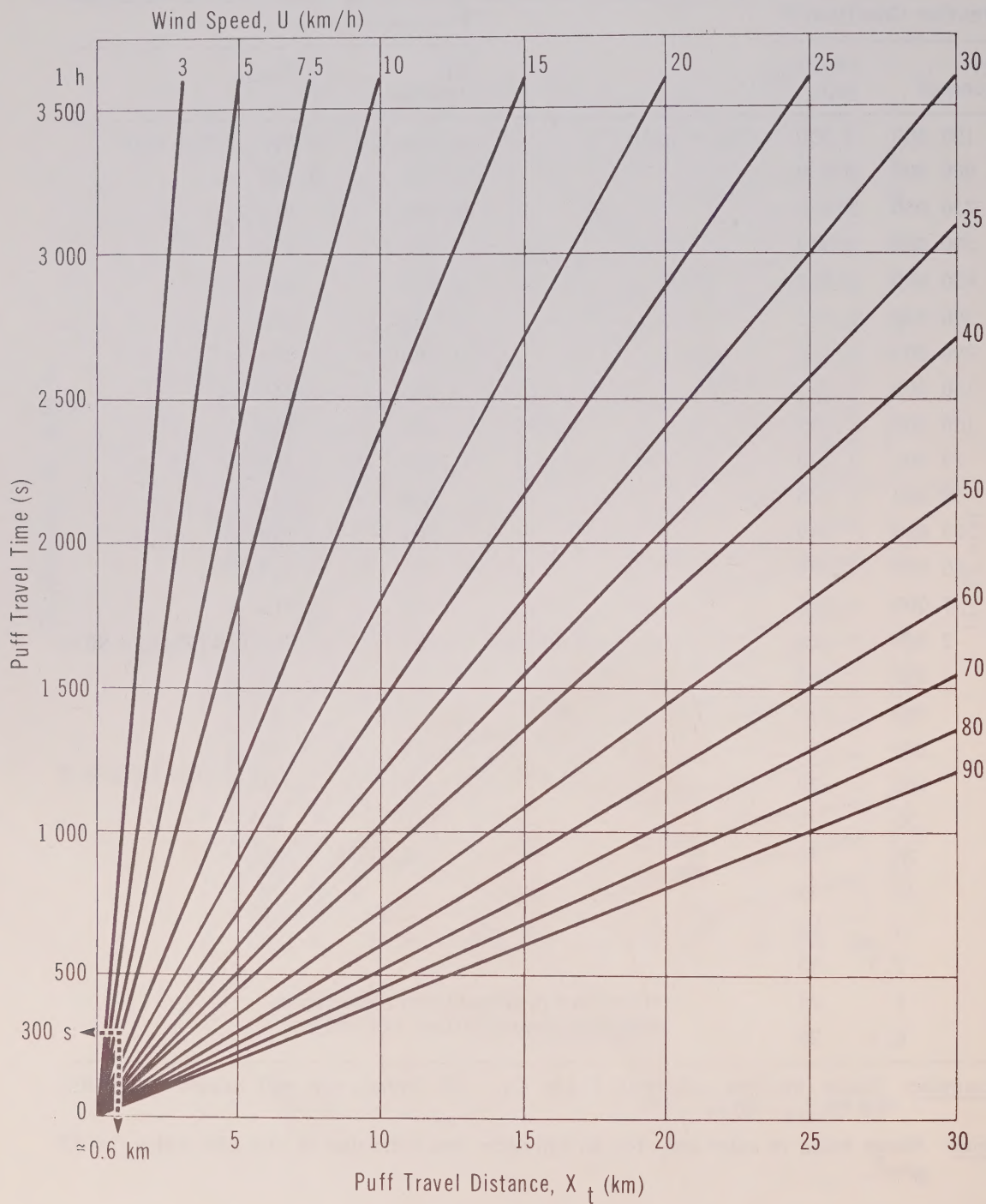
Weather Condition D			Weather Condition F		
Q_T (tonnes)	$(W/2)_{\max}$ (m)		Q_T (tonnes)	$(W/2)_{\max}$ (m)	
1 100 000	3 990	(98.4 km)*	50 000	1 820	(97.1 km)*
1 000 000	3 850		25 000	1 360	
750 000	3 450		10 000	915	
500 000	2 950		7 500	810	
400 000	2 710		5 000	680	
300 000	2 430		2 000	460	
200 000	2 080		1 500	410	
150 000	1 865		1 000	350	
100 000	1 595		750	315	
75 000	1 430		500	270	
50 000	1 225		250	205	
25 000	940		200	190	
10 000	670		100	145	
5 000	520		50	110	
2 000	370	$Q_T = 20 \text{ tonnes} \rightarrow$	20	80	$\rightarrow (W/2)_{\max} = 80 \text{ m}$
1 000	285		10	60	
500	220		7.5	55	
250	170		5	45	
100	120		2.5	35	
50	95		1	25	
20	70		0.5	20	
10	55				
5	45				
2.5	35				
1	25				
0.5	20				

*Data are provided up to a maximum downwind hazard distance of 100 km.

Example: Under weather condition F and $Q_T = 20 \text{ tonnes}$, the puff hazard half-width $(W/2)_{\max} = 80 \text{ m}$

Note: Above table is valid only for an ethylene concentration of the LFL value, or 35 g/m^3 .

ETHYLENE

**PUFF TRAVEL TIME
VS TRAVEL DISTANCE**

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_T) can be determined which indicates how far downwind the puff has travelled.

5.3.3 Sample Calculation. The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of ethylene. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill quantity) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of ethylene were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution:

Step 1: Quantity spilled is given $Q_T = 20$ tonnes

$$\cdot \quad Q_T = 2 \times 10^7 \text{ g}$$

Step 2: Determine the wind speed (U) and direction (D)

• Use available weather information, preferably on-site observations

• Given: $U = 7.5 \text{ km/h}$, then $U = 7.5 \div 3.6 = 2.1 \text{ m/s}$

$D = \text{NW or } 315^\circ$ (D = Direction from which wind is blowing)

Step 3: Determine the weather condition

• From Table 5, weather condition is F since U is less than 11 km/h and it is night

Step 4: Determine the hazard concentration limit (C)

• This is the lower of the asphyxiation level or the LFL, so for ethylene

$$C = 35 \text{ g/m}^3 \text{ (LFL = } 35 \text{ g/m}^3 \text{; asphyxiation level = } 190 \text{ g/m}^3 \text{)}$$

Step 5: Compute C/Q_T

$$\cdot \quad C/Q_T = \frac{35}{2 \times 10^7} = 1.75 \times 10^{-6} \text{ m}^{-3}$$

Step 6: Calculate the hazard distance (X) from the instantaneous point source

• From Figure 10, with $C/Q_T = 1.75 \times 10^{-6} \text{ m}^{-3}$ and weather condition F, $X \approx 2.6 \text{ km}$

- Step 7: Calculate the puff hazard half-width $(W/2)_{\max}$
- Use Table 6
 - With $Q_T = 20$ tonnes
 - Then for weather condition F, $(W/2)_{\max} = 80$ m
- Step 8: Determine the time since spill
- $t = 5 \text{ min} \times 60 = 300 \text{ s}$
- Step 9: Calculate the distance travelled (X_t) by the vapour puff since the time of the accident
- Using Figure 12, with $t = 300 \text{ s}$ and $U = 7.5 \text{ km/h}$, then $X_t = 0.6 \text{ km}$ (more accurately from $X_t = Ut = 2.1 \text{ m/s} \times 300 \text{ s} = 630 \text{ m} = 0.63 \text{ km}$)
- Step 10: Map the hazard zone
- This is done by drawing a rectangular area with dimensions of twice the maximum puff hazard half-width (80 m) by the maximum hazard distance downwind of the instantaneous point source (2.6 km) along the direction of the wind, as shown in Figure 13
 - If the wind is reported to be fluctuating by 20° about 315° (or from $315^\circ \pm 10^\circ$), the hazard zone is defined as shown in Figure 14
 - Note that the puff has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h there remain 16 minutes before the puff reaches the maximum downwind hazard distance of 2.6 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on water, liquefied ethylene will vaporize and at the same time will spread on the surface. Because it is relatively insoluble, little ethylene will be lost from the pool by dissolution. For the purposes of nomogram preparation, the extent of spread on the surface of the water has been estimated, accounting for the loss due to vaporization.

The rate of spreading on water is based on the balance of forces tending to spread the liquid (gravity and surface tension) and those tending to resist spreading (inertial and viscous forces). Since cryogenic liquids, such as ethylene, are evaporated quickly, only the initial gravity-inertia regime of spread is considered relevant (Raj 1974). The maximum size of the spill pool depends to a large extent on the rate of vaporization.

The equations representing the spreading of the spill on water are presented in the Introduction Manual. For the purposes of the nomogram presented, the water temperature has been taken at 20°C , representing a reasonable maximum for surface water bodies. This condition maximizes the spill size.

ETHYLENE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

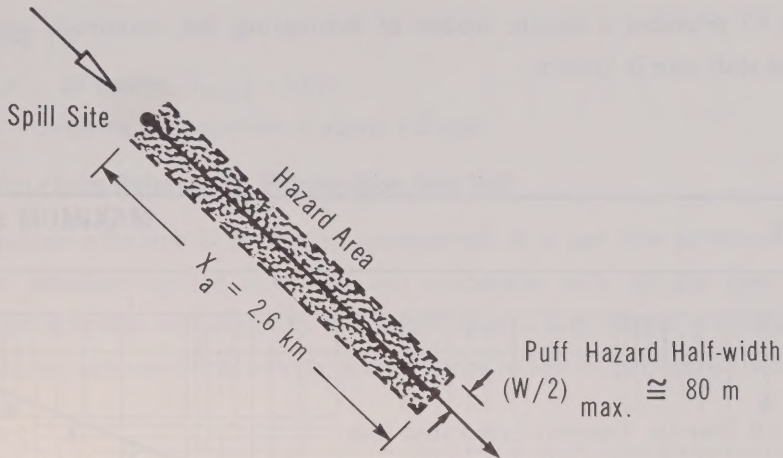
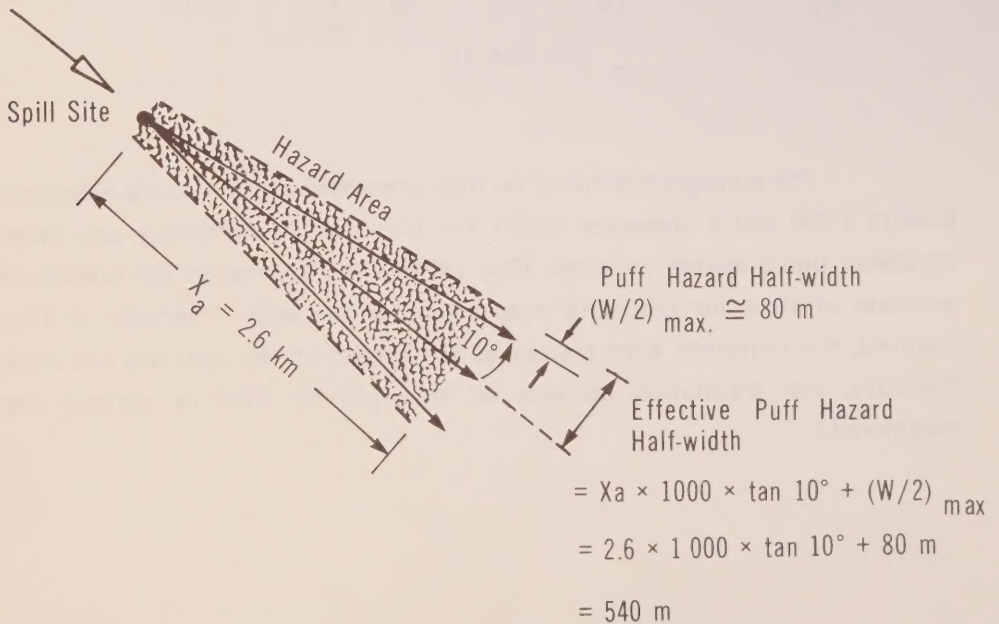
Wind $U = 7.5$ km/h from 315° (NW)

FIGURE 14

ETHYLENE

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM

Wind $U = 7.5$ km/h from $315^\circ \pm 10^\circ$ 

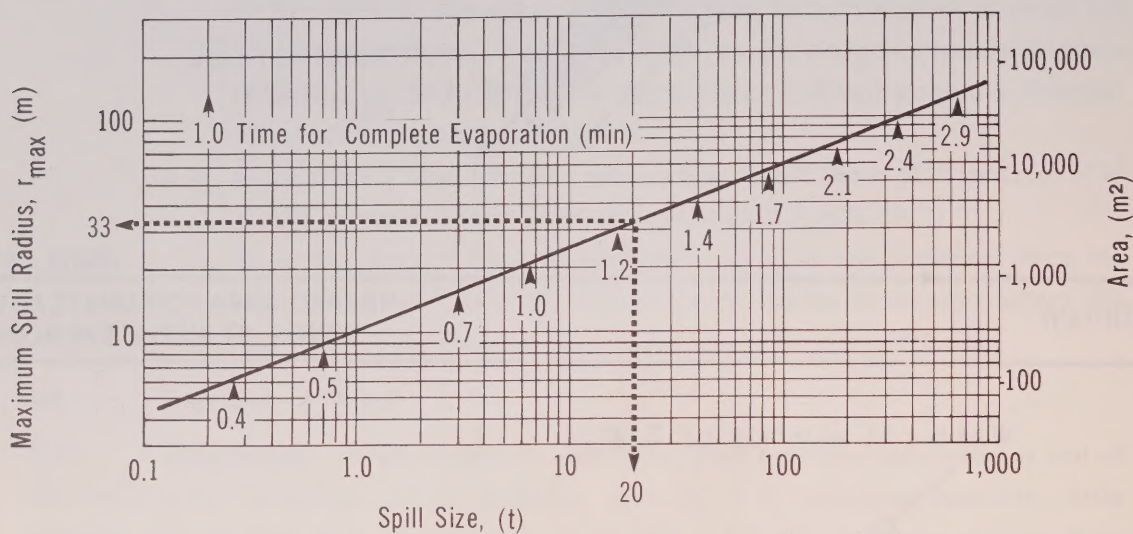
5.4.2 Nomogram for Spreading on Still Water. The following nomogram is presented to simplify the calculation of spreading on still water (without dissolution) and to estimate the time for complete evaporation for a range of spill sizes.

5.4.2.1 Figure 15: Maximum spill radius versus spill size. Assuming no dissolution in water, Figure 15 provides a simple means of estimating the maximum spill radius for ethylene, if the spill size is known.

FIGURE 15

**MAXIMUM SPILL RADIUS
VS SPILL SIZE**

LIQUEFIED ETHYLENE



The nomogram is based on data presented in the Hazard Assessment Handbook (CHRIS 1978) and a computer model for simultaneous spreading and evaporation of a cryogenic liquid spilled on water (Raj 1974). The figures on the nomogram provide an estimate of time for complete evaporation of the spill. Because of the short times involved, the complete time history of the spread of the spill has not been considered. Similarly, the translation distance of the spill by wind or surface current is not considered.

5.4.3 Sample Calculation. A 20 tonne spill of ethylene has occurred on a large lake. What is the maximum size of the spill (assuming no dissolution) and approximate time for complete evaporation?

Solution

- Use Figure 15
- With mass = 20 tonnes, $r_{\max} = 33$ m
- Time for complete evaporation is about 1.2 min

5.5 Subsurface Behaviour: Penetration into Soil

Because ethylene is primarily transported as a gas (via pipeline) and because even liquefied ethylene spilled onto soil will evaporate very quickly (see above), it is unlikely that an ethylene release onto soil would pose a significant groundwater hazard. Because of this, no assessment of ethylene movement in soil is considered necessary.

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. The maximum acceptable concentration of ethylene in drinking water has been set at 0.5 mg/L in Europe (Verschuereen 1977).

6.1.2 Air. Ambient air quality limits of $575 \mu\text{g}/\text{m}^3$ (0.5 ppm) for 1 hour and $115 \mu\text{g}/\text{m}^3$ (0.1 ppm) for 8 hours have been set in California (PB 83-107748). Similar ambient air quality limits have been set in the provinces of Ontario and Alberta. Russia has set an ambient air quality limit at $3000 \mu\text{g}/\text{m}^3$ (3.3 ppm for 24 hours) (Verschuereen 1977).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Ethylene has been assigned a TL_{m96} of 1000 to 100 mg/L (RTECS 1979).

6.2.2 Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Fish Kill Data</u>					
22 to 25	1	Sunfish	killed		WQCDB-1 1970

6.3 Toxicity to Other Biota

6.3.1 Terrestrial Plants. Terrestrial plants show a wide disparity in response to ethylene, leading to a classification of plants as either resistant or sensitive. It has been shown that concentrations that cause serious effects to sensitive plants may have no or even apparently beneficial effects on resistant plants. Fruits produce ethylene as a ripening agent and ethylene is occasionally used as a ripening agent (treated at 2 to 20 ppm ethylene). Natural production of ethylene by apples is about $100 \mu\text{L}/\text{kg}/\text{h}$, by pears about 30 to $120 \mu\text{L}/\text{kg}/\text{h}$, and by peaches about $40 \mu\text{L}/\text{kg}/\text{h}$. Vegetation damage attributed to ethylene is often associated with industrial plants but also with car exhaust (about 14 percent of emitted hydrocarbons are ethylene) and burning of organic wastes (production of about 0.5 kg per tonne garbage). Plants that are resistant to ethylene include grasses and grassy vegetables such as lettuce. Shrubs such as roses often show a

high temperature dependence with their sensitivity to ethylene. Roses, in one study, displayed petal drop at 10 ppm ethylene at high temperatures (20°C); at low temperatures (5°C), the same effect was noted at 40 ppm. Sensitive plants, those showing injury at levels as low as 0.1 ppm, include several species of flowers (orchids, carnations, etc.) and a number of vegetables such as tomatoes, potatoes, peppers, beans and peas (PB 83-107748; Verschueren 1977).

The effects on sensitive species include (PB 83-107748):

1. growth retardation,
2. epinasty (downward curvature of leaves and growth area),
3. the abscission of leaves, buds and flowers,
4. irregular opening of flowers,
5. splitting of leaves and flowers,
6. inhibition of elongation and preferential swelling of stems,
7. fading of flowers,
8. blanching of chlorophyll,
9. hastening of fruit ripening and coloration, and
10. loss of ability to orient properly with gravity.

Studies on sensitive species have shown that ethylene levels of 0.5 to 4 ppm cause leaf loss and of 0.1 to 0.5 ppm cause growth retardation or inhibition of flowering (ERM 1982). Ethylene concentrations of 0.5 ppm have injured vegetable crops (Yopp 1974). Other effects noted include the reduction of photosynthesis (Kays 1980), acceleration of ripening (Lipton 1979), effects on sprout growth, leaf growth, root growth and germination (Minato 1979; Konings 1979; Lee 1979; Jackson 1981; Masuda 1980; Marousky 1979; Taylorson 1979; Schonbeck 1980; Egley 1980). The effects of ethylene are attributed to its action as a growth regulator, which appears to be applicable to many phases of a plant's development (Blomstrom 1980).

The following effects were noted in various studies (Verschueren 1977):

Species	Concentration (ppm)	Exposure time (h)	Effects
<i>Vanda orchid</i>	1	24	Fading of flowers
<i>Antirrhinum majus</i>	0.5	1	Abscission of flowers
<i>Cattleya orchid</i> , buds	0.01	24	Sepal tissue collapse
	0.056	6	
	0.3	1	

Species	Concentration (ppm)	Exposure time (h)	Effects
<i>Cattleya orchid</i>	0.002 0.1	24 8	Sepal tissue collapse
<i>Chenopodium album</i>	0.05		Epinasty
<i>Dianthus caryophyllus</i>	0.10	6	Inhibited flower opening
<i>Fagopyrum sagittatum</i> (<i>F. esculentum</i>)	0.05		Epinasty
<i>Gossypium hirsutum</i>	0.6	720	Reduction in growth and yield
<i>Itelanthus annuus</i>	0.05		Epinasty
<i>Lathyrus odoratus</i>	0.2	72	Epinasty
<i>Lilium regale</i>	4.0		Growth retardation and epinasty
<i>Lycopersicon esculentum</i>	0.1	48	Growth retardation
<i>Narcissus</i> species	2.0 4.0	72 72	Growth retardation Growth retardation and leaf curl
<i>Rosa</i> species	0.33 10.0 40.0 40.0 40.0	120 24 24 48 168	Epinasty and leaf abscission at room temperature Petal fall at 70°F, none at 32°F, 40°F and 50°F Epinasty at 70°F Epinasty and leaf abscission at 70°F No abscission at 41°F
<i>Solamon tuberosum</i>	0.05	16	Epinasty
<i>Tagetes patula</i>	0.05		Epinasty
<i>Tulipa gesneriana</i>	4.0		Leaf roll
Tomato	0.1 0.04	48 3-4	Leaf epinasty Leaf epinasty of mature leaves
African marigold	0.001		Leaf epinasty
Lemon	0.025-0.05		Epinasty
<i>Datura stramonium</i>	0.1		Close to limit for response
<i>Lycopersicum esculentum</i>	0.2		Epinasty of leaves

Species	Concentration (ppm)	Exposure time (h)	Effects
<i>Begonia luminosa</i>	8		Slight epinasty
Sweet pea	0.1		Inhibited elongation of the epicotyl
	0.4		Production of triple response; horizontal mutation and swelling

6.4 Long-term Fate and Effects

The gas will disperse quite rapidly. There is no bioaccumulation or food chain contamination potential.

7 HUMAN HEALTH

Ethylene has been designated as a simple asphyxiant by the USA-ACGIH. It has been reported in the EPA TSCA Inventory.

No data were found concerning the chemical's reproductive or carcinogenic effects. No mutagenic properties were found when *E. coli* and several species of *Bacillus* were studied. In one study, no increased incidence of tumours was found in animals exposed to ethylene for 24 months (Chem. Eng. 1980).

The toxicological data summarized here have been extracted from reliable standard reference sources and are representative of information in the literature. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations.

7.1 Recommended Exposure Limits

The exposure standards for ethylene are based upon its asphyxiant properties. Canadian provincial guidelines generally are similar to those of the USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Simple Asphyxiant	USA-ACGIH	1000 ppm (suggested for for asphyxiants)	Patty 1981
Simple Asphyxiant	USA-ACGIH	Minimum oxygen content should be 18% by volume under normal conditions	TLV 1983
Asphyxiant Simple	Quebec	Minimum oxygen content should be 19.5% by volume under normal conditions	Quebec 1979
8 h	USA-California	MIC - 0.13 mg/m ³ (0.1 ppm)	Verschueren 1977
24 h	USSR (also Bulgaria and Yugoslavia)	MIC - 3 mg/m ³ (2.3 ppm)	Verschueren 1977
24 h	Israel - tentative	MIC - 0.26 mg/m ³ (0.2 ppm)	Verschueren 1977
<u>Short-term Exposure Limits (STEL)</u>			
1 h	USA-California	MIC - 0.62 mg/m ³ (0.5 ppm)	Verschueren 1977
20 min	USSR	MIC - 3 mg/m ³ (2.3 ppm)	Verschueren 1977
30 min	Israel - tentative	MIC - 0.65 mg/m ³ (0.5 ppm)	Verschueren 1977

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
Unspecified	Ethylene is a nonirritant to the skin	Patty 1981
Unspecified	No appreciable hazard. Practically harmless to the skin	CHRIS 1978

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
Unspecified	Vapours are not irritating to the eyes	AAR 1981

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristics: Faint, sweet, slight ethereal odour (AAR 1981). Unpleasant, oleophinic odour (Verschueren 1977).

Odour Index: 57 100 (Verschueren 1977).

Parameter	Media	Concentration	Reference
Upper Recognition Threshold	In air	700 ppm	AAR 1981
Threshold Odour Concentration	In air	400 ppm	AAR 1981
Odour Threshold	-	20 mg/m ³	Patty 1981
Median Recognition Threshold	In air	400 ppm	AAR 1981
Absolute Odour Threshold	In air	260 ppm	AAR 1981
Recognition Threshold	In air	4 000 ppm	ASTM 1980
Detection Threshold	In air	260 ppm	ASTM 1980

7.3.2 Taste. Garlic-like (CCPA 1982).

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Human		
85 (percent vol.)	Instant loquacity Instant paralytic reaction Near instant incoordination Faintness in 55 s	ITII 1981 AAR 1981
51 (percent vol.)	Paralytic reaction in 40 s Loquacity in 75 s Incoordination in 8 to 9 min	AAR 1981
50 (percent vol.)	Loss of consciousness Death (8 percent O ₂)	Patty 1981
47 (percent vol.)	Loquacity in 120 s Paralytic reaction in 60 s Incoordination in 12 min	ITII 1981 AAR 1981
37.5 (percent vol.)	Memory disturbances after 15 min	Patty 1981
SPECIES: Mammal		
950 000 ppm	LC _{LO}	AAR 1981
SPECIES: Dog		
1.4 (percent vol.)	Anesthetic in 2 to 8.2 min	Patty 1981
SPECIES: Rat		
10 000, 25 000 and 37 000 ppm (4 h)	Increased serum pyruvate and increased liver weights	Patty 1981
11 500 mg/m ³ (10 000 ppm)	No apparent effect on growth rate	PB 83-107748

Exposure Level (and Duration)	Effects	Reference
SPECIES: Mouse		
950 000 ppm	Lethal concentration	AAR 1981
95 pph	LC ₅₀	AAR 1981
<u>Chronic Exposures</u>		
SPECIES: Rat		
3 mg/m ³ /d (90 d)	Hypotension, disruption of the subordination chronaxy and inhibited cholinesterase activity	Patty 1981

7.4.2 Ingestion. No data.

7.4.3 Mutagenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: <i>E. coli</i>		
Unspecified	No mutagenic properties shown	Patty 1981
SPECIES: <i>Bacillus</i> (unspecified)		
Unspecified	No mutagenic properties shown	Patty 1981

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Drowsiness (AAR 1981).
2. Dizziness (AAR 1981).
3. Headaches (AAR 1981).

4. Muscular weakness (AAR 1981).
5. Unconsciousness (AAR 1981).
6. Reversible depression of the central nervous system (AAR 1981).
7. Malfunction of the heart (ITII 1981).
8. Respiratory paralysis (AAR 1981).
9. Death (AAR 1981).

7.5.2 Ingestion. Ingestion is unlikely as ethylene is a gas under normal atmospheric conditions.

1. Liquid form is irritating if ingested (Lefèvre 1980).

7.5.3 Skin Contact.

1. Exposure to liquid form could cause frostbite due to rapid evaporation (AAR 1981).

7.5.4 Eye Contact.

1. Vapour is not irritating to eyes (CHRIS 1978).

7.6 Human Toxicity to Decay or Combustion Products

7.6.1 Carbon Dioxide. Carbon dioxide is a colourless, odourless gas which, in elevated concentrations, may act to produce mild narcotic effects, respiratory stimulation and asphyxiation. Its TLV* is 5000 ppm (8 h-TWA) and 15 000 ppm (STEL) (TLV 1983).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Ethylene with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP												SPECIFICS	REFERENCE
	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION	FORMATION OF TOXIC FUMES	OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION		
GENERAL													
Heat		x	x										Sax 1979; Bretherick 1979
High Temperature and Pressure				x							When initiated by shock		Matheson 1980
Fire		x	x								Moderate explosion hazard		Sax 1979
SPECIFIC CHEMICALS													
Aluminum Chloride									x		Violent reaction may occur		NFPA 1978
Benzoyl Peroxide and Carbon Tetra- chloride			x								Mixture of the three explodes		Bretherick 1979
Bromotrichloro- methane			x								Mixture may explode when heated		Bretherick 1979
Carbon Tetrachlo- ride			x								Can explode under high pressure in the presence of organic per- oxides		Bretherick 1979; NFPA 1978
Chlorine			x								Explodes if initiated by sunlight or ultra- violet radiation		Bretherick 1979

8.1 Compatibility of Ethylene with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION FIRE EXPLOSION FORMATION OF FLAMMABLE GASES VIOLENT POLYMERIZATION DECOMPOSITION FORMATION OF TOXIC FUMES OF GREATER TOXICITY PRESSURIZATION IN CLOSED SOLUBILIZATION VIOLENT REACTION NON-HAZARDOUS REACTION											SPECIFICS	REFERENCE
Nitrogen Dioxide			x									Forms unstable nitrosates and nitrosites which may explode	NFPA 1978
Ozone			x									May be explosive	Bretherick 1979
Sulphur Monochloride					x							Forms mustard gas (di(2-chloro-ethyl)sulphide)	Matheson 1980
Tetrafluoroethylene			x							x		Explosive when heated at 160°C and high pressure	Bretherick 1979
Trifluoromethyl Hypofluorite			x									Explosive on mixing	Bretherick 1979
<u>CHEMICAL GROUPS</u>													
Organic Peroxides	x				x								EPA 600/2-80-076
Oxidizing Agents		x										Exhaustive oxidation can result in ignition of the hydrocarbon	EPA 600/2-80-076
Halogens							x					Forms dihalides	Matheson 1980

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Ethylene is an extremely flammable gas (NFPA 1978). Its vapours spread along the ground from the spill, and flashback may occur (ERG 1980). Containers may explode when heated (ERG 1980). Stop flow of gas before applying extinguishing agents.

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to prevent rupture. Stop flow of gas before applying extinguishing agents wherever possible.

Small Fires: Dry Chemical or CO₂

Large Fires: Water spray, fog or foam

Move containers away from fire area if this can be done without risk. Stay away from tank ends. For massive fires, use unmanned hose holder or monitor nozzles (ERG 1980).

9.1.3 Evacuation. In the event of an explosion, the minimum safe distance from flying fragments is 600 m in all directions. Keep internal combustion engines and other sources of ignition from immediate area (EAG 1978).

9.1.4 Spill Actions, Cleanup and Treatment.

9.1.4.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition (Dow ERIS 1979).

9.1.4.2 Spills on land. Ethylene will rapidly disperse. Little can be done for removal, etc.; however, little residual ethylene will be present. Traffic and other sources of ignition should be eliminated until concentrations are well below the flammability limit.

9.1.4.3 Spills on water. Ethylene will rapidly disperse as a vapour cloud. If ethylene concentrations are of concern in the water, these may be reduced by aeration. If water containing ethylene is used for a water supply, there is concern that chlorination can produce dichloroethane. Aeration of water before chlorination can reduce the ethylene concentration to a very low level (OHM-TADS 1981).

9.1.5 Disposal. In spill situations, it is rather unlikely that waste ethylene is present. Residual amounts in containers can be returned to the manufacturer (OHM-TADS 1981).

9.1.6 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be ethylene:

- Full protective clothing and self-contained breathing apparatus should be worn until low concentrations are established (Dow ERIS 1979).
- Chemical workers' goggles, hard hat, rubber gloves and rubber boots should also be worn (Dow ERIS 1979).

9.1.7 Storage Precautions. Protect containers against physical damage. Isolate from oxygen, chlorine, and oxidizing materials. Store in cool, well-ventilated area, of noncombustible construction, away from possible sources of ignition. Protect against static electricity and lightning. Outside or detached storage is preferred (NFPA 1978).

10

PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

Although spills of this material have been recorded, no significant information regarding cleanup methods or response has been documented.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Method for the Detection of Ethylene in Air

11.1.1 Gas Chromatography (CCPA 1982). A range of 10 to 10 000 mg/m³ of ethylene in air may be determined using direct injection technique for gas chromatographic analysis.

A large volume (10 mL sample loop) of air is injected directly into a gas chromatograph equipped with a flame ionization detector.

Typical gas chromatograph conditions are a 6 ft. x 1/8 in. stainless steel column packed with Alumina F-1 60/80 mesh. (Nitrogen carrier gas flow at 20 mL/min, airflow at 250 mL/min, hydrogen flow at 20 mL/min, injector temperature at 150°C, detector temperature 150°C, and column temperature of 90°C.) The ethylene is then determined by an electronic integrator in connection with a standard curve.

11.2 Quantitative Method for the Detection of Ethylene in Water

11.2.1 Partition Infrared (AWWA 1981). A range of 11.34 to 113.40 ppm ethylene may be determined in water using a partition infrared method which is suitable for a variety of organic compounds.

A minimum of 1 L of representative sample is collected in an appropriate container and acidified to pH 2 or lower with dilute hydrochloric acid. A 5 mL volume of acid should be sufficient. The sample is transferred to a separatory funnel and a 30 mL volume of Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is added after it is used to rinse the sample container. The solvent layer is drained into a 100 mL volumetric flask. Two more 30 mL Freon® 113 extracts are carried out and the extracts combined in the 100 mL volumetric flask. The volume is adjusted to 100 mL with Freon® 113. The sample is scanned on a suitable infrared spectrophotometer from 3000 to 900 cm^{-1} using matched 1 cm cells. The concentration is determined from a calibration curve.

11.3 Qualitative Method for the Detection of Ethylene in Water

The sample is collected as in Section 11.2.1. Two drops of sample are placed in a dry test tube and a 1 percent solution of bromine in carbon tetrachloride is added drop-wise. De-coloration of the bromine solution indicates the presence of an alkene (Owen 1969).

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Common Abbreviations

BOD	biological oxygen demand	MMAD	mass median aerodynamic diameter
b.p.	boiling point	MMD	mass median diameter
CC	closed cup	m.p.	melting point
cm	centimetre	MW	molecular weight
CMD	count median diameter	N	newton
COD	chemical oxygen demand	NAS	National Academy of Sciences
conc.	concentration	NFPA	National Fire Protection Association
c.t.	critical temperature	NIOSH	National Institute for Occupational Safety and Health
eV	electron volt		
g	gram		
ha	hectare		
Hg	mercury		
IDLH	immediately dangerous to life and health	nm	nanometre
Imp. gal.	Imperial gallon	o	ortho
J	Joule	OC	open cup
kg	kilogram	p	para
kJ	kilojoule	P _c	critical pressure
km	kilometre	PEL	permissible exposure level
kPa	kilopascal	pH	measure of acidity/alkalinity
kt	kilotonne	ppb	parts per billion
L	litre	ppm	parts per million
lb.	pound	P _s	standard pressure
LC ₅₀	lethal concentration fifty	psi	pounds per square inch
LC _{LO}	lethal concentration low	s	second
LD ₅₀	lethal dose fifty	STEL	short-term exposure limit
LD _{LO}	lethal dose low	STIL	short-term inhalation limit
LEL	lower explosive limit	T _c	critical temperature
LFL	lower flammability limit	TC _{LO}	toxic concentration low
m	metre or meta	T _d	decomposition temperature
M	molar	TD _{LO}	toxic dose low
MAC	maximum acceptable concentration	TL _m	median tolerance limit
max	maximum	TLV	Threshold Limit Value
mg	milligram	T _s	standard temperature
MIC	maximum immission concentration	TWA	time weighted average
min	minute or minimum	UEL	upper explosive limit
mm	millimetre	UFL	upper flammability limit
		VMD	volume mean diameter
		v/v	volume per volume
		w/w	weight per weight
μg	microgram		
μm	micrometre		
°Be	degrees Baumé (density)		

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